

The Garfield and Uley nontronites – An infrared spectroscopic comparison

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Abstract:

FTIR and Infrared emission spectroscopy (IES) has been used to characterise the Uley (Australian) and Garfield nontronites. These clay minerals are characterised by a strong emission band at 3570 cm^{-1} attributed to the FeFeOH unit.

Dehydroxylation is followed by the loss of intensity of this band as a function of temperature. Dehydroxylation is also followed by the loss of intensity of the FeFeOH deformation vibration at 843 cm^{-1} . IES shows that the dehydroxylation occurs as a continuous process in comparison to DTA/TGA studies where the dehydroxylation occurs abruptly at $425\text{ }^{\circ}\text{C}$. Water in these high iron bearing smectites have been observed through the stretching mode at 3430 cm^{-1} and the

bending mode at 1630 cm^{-1} . Different types of water are identified in the nontronite structure by the analysis of the band profile in the 1590 to 1680 cm^{-1} region. Low frequency vibrations show that the Uley green nontronite is similar to the Garfield nontronite. The brown Uley nontronite is closer to the Hohen-Hagen nontronite. The Uley nontronites may therefore be used spectroscopically to replace other nontronites as a reference clay mineral.

Key words: dehydroxylation, FT-IR, infrared emission spectroscopy, montmorillonite, nontronite, smectite.

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1. Introduction

Smectites belong to the group of clay minerals, which expand upon contact with water [1]. The presence of the water influences the physio-chemical properties for example the rheology of the clays [2]. Smectites may be either dioctahedral or trioctahedral, depending on whether the octahedral layer is filled with 2 out of 3 positions with a trivalent cation or fully filled with a divalent cation [3]. The dioctahedral smectites can be divided into two principal groups (a) aluminian smectites and (b) the iron-rich varieties including ferruginous smectites and nontronites. Two types of dioctahedral smectites exist depending on the site of the layer charges: (a) montmorillonites where the charge arises from divalent cations usually Mg replacing the M^{3+} cations in the octahedral sites resulting in a diffuse layer charge, and (b) beidellites where the strongly localised charge arises from the Al^{3+} substitution into the Si^{4+} tetrahedral sites [1,3]. In iron-rich (ferruginous) smectites and nontronites, some or all of the Al in the octahedral layer is replaced with ferric iron (Fe^{3+}). In the case of the ferruginous smectites the theoretical structural formula can be given by $(M^{++}_{x/2}.nH_2O)(Fe^{3+}_4)(Si_{8-x}Al_x)O_{20}(OH)_4$ [1,4]. This clay formula as written is the end member and is known as nontronite. Montmorillonites and beidellites generally have $Fe^{3+} < 1\%$ [5,6]. The term ferruginous smectites (or Ferrian smectites) is used for dioctahedral smectites when when Fe^{3+} is $> 3\%$ [1]. Ferruginous smectites have partial substitution of the aluminum by iron, whereas nontronites have total replacement.

The ideal structural formula for aluminian smectites is

$(\text{Al}_{3.15}\text{Mg}_{0.85})(\text{Si}_{8.0})\text{O}_{20}(\text{OH})_4\text{X}_{0.85}\cdot n\text{H}_2\text{O}$. X in the formula is a monovalent cation which counterbalances the layer charges. Structural formulae of clay minerals may be used to characterise these minerals. However non-monomineralic compositions may lead to distortion of these formulae [7]. Therefore to determine the structure a combination of chemical, diffraction and spectroscopic methods should be used. Diffraction methods provide information on the unit cell and long range ordering [8], yielding information on the average structure but not of the composition. For poorly diffracting minerals such as the nontronites, spectroscopic methods are much more useful. Methods such as infrared spectroscopy, Raman spectroscopy and nuclear magnetic resonance provide information about short range ordering and molecular structures.

Infrared spectroscopy has been used for a long period of time to study clay minerals [9-11]. In particular, infrared absorption techniques have been extensively used for the study of nontronites and other iron bearing clay minerals [see for example references 12-17]. One of the difficulties of using infrared KBr pellet absorption techniques is the possibility of exchange of the counter ions of the smectites with the potassium of the KBr discs which are made under pressure. Other absorption techniques such as self-supporting films and deposits on windows avoid this difficulty. Both the techniques of diffuse reflectance (DRIFT) and infrared emission spectroscopy (IES) also avoid this difficulty. Infrared emission spectroscopy allows the possibility of studying the dehydroxylation and phase changes of minerals at elevated temperatures. The technique of measurement of discrete vibrational frequencies *emitted* by thermally excited molecules, known as Fourier transform Infrared Emission

Spectroscopy (FTIR ES), has not been widely used for the study of mineral structures [see for example references 18-22]. The major advantages of IES are that the samples are measured *in situ* at *elevated temperatures* and IES requires no sample treatment other than making the smectite sample of submicron particle size. Most of the smectite samples studied are of this size naturally. Further, the technique removes the difficulties of heating the sample to dehydroxylation temperatures and quenching before measurement, as IES measures the dehydroxylation process as it is actually taking place. Here in this paper we report the changes in the infrared spectrum upon thermal treatment of a series of nontronites using the FTIR ES technique.

2. Materials and Methods

2.1 Nontronite Clay Minerals.

The clay minerals used are the wards Natural Science establishment: Garfield nontronite from Whitman County, Washington, USA labelled as API-H33a, or sometimes #33a [23], and Clay Mineral Society standard: the nontronite NG-1 from Hohen-Hagen, Germany [24]. This latter nontronite is no longer obtainable and there is a need for a nontronite clay to replace this standard. The two Australian samples are from Uley Graphite Mine, Eyre Peninsula, South Australia. The calcium exchanged, < 2 μm portions, were used [25]. Samples were analysed for purity by X-ray diffraction. Infrared spectroscopy was also used to detect low levels of other phases, particularly kaolinite and amorphous phases. The Uley green nontronite (NAu-1) sample contained traces of kaolinite and the Uley brown nontronite (NAu-2)

contained calcite and ferrihydrite. The contaminants were at very low levels and were not detected by XRD.

The Garfield nontronite has a formula $(M^{+1.07})[Al_{0.23}Fe_{3.71}Mg_{0.03}][Si_{7.03}Al_{0.97}]O_{20}(OH)_4$ (Manceau et al., 2000a,b). The nontronite from Hohen Hagen, Germany (CMR NG-1) has a structural formula: $(M^{+0.95})[Al_{0.86}Fe_{3.08}Mg_{0.05}][Si_{7.12}Al_{0.11}Fe_{0.76}]O_{20}(OH)_4$. The Uley Green (NAu-1) nontronite has a formula of $[M^{+1.05}][Al_{0.26}Fe_{3.71}Mg_{0.03}][Si_{6.97}Al_{1.03}]O_{20}(OH)_4$ and the Uley brown (NAu-2) nontronite has a formula of $[M^{+0.83}][Al_{0.42}Fe_{3.43}Mg_{0.04}][Si_{7.52}Al_{0.06}Fe_{0.42}]O_{20}(OH)_4$. Nontronites contain Fe predominantly in the trivalent state [26-29] The above analyses were based upon the results conducted on ignited, Ca-saturated purified fractions (nominally $<0.2 \mu m$) of each nontronite.

2.2 *Infrared Absorption Spectroscopy.*

Absorption spectra were obtained using a Perkin-Elmer Fourier transform infrared spectrometer (2000) equipped with a TGS detector. Spectra were recorded by accumulating 1024 scans at 4 cm^{-1} resolution and a mirror velocity of 0.3 cm/sec in the mid-IR.

2.3 *Infrared Emission Spectroscopy.*

FTIR emission spectroscopy was carried out on a Digilab FTS-60A spectrometer equipped with a TGS detector, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission

experiment have been published elsewhere [18]. Approximately 0.2 mg of dried nontronite was spread as a thin layer (approximately 0.2 microns) on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating. The infrared emission cell consists of a modified atomic absorption graphite rod furnace, which is driven by a thyristor-controlled AC power supply capable of delivering up to 150 amps at 12 volts. A platinum disk acts as a hot plate to heat the smectite sample and is placed on the graphite rod. An insulated 125- μm type R thermocouple was embedded inside the platinum plate in such a way that the thermocouple junction was <0.2 mm below the surface of the platinum. Temperature control of $\pm 2^\circ\text{C}$ at the operating temperature of the smectite sample was achieved by using a Eurotherm Model 808 proportional temperature controller, coupled to the thermocouple. The design of the IES facility is based on an off axis paraboloidal mirror with a focal length of 25 mm mounted above the heater capturing the infrared radiation and directing the radiation into the spectrometer. The assembly of the heating block, and platinum hot plate is located such that the surface of the platinum is slightly above the focal point of the off axis paraboloidal mirror. By this means the geometry is such that approximately 3 mm diameter area is sampled by the spectrometer. The spectrometer was modified by the removal of the source assembly and mounting a gold-coated mirror, which was drilled through the centre to allow the passage of the laser beam. The mirror was mounted at 45° , which enables the IR radiation to be directed into the FTIR spectrometer.

In the normal course of events, three sets of spectra are obtained: firstly the black body radiation over the temperature range selected at the various temperatures, secondly the platinum plate radiation is obtained at the same temperatures and thirdly

the spectra from the platinum plate covered with the sample. Normally only one set of black body and platinum radiation is required. The emittance spectrum at a particular temperature was calculated by subtraction of the single beam spectrum of the platinum backplate from that of the platinum + sample, and the result ratioed to the single beam spectrum of an approximate blackbody (graphite). This spectral manipulation is carried out after all the spectral data has been collected. The emission spectra were collected at intervals of 50°C over the range 200 - 750 °C. The time between scans (while the temperature was raised to the next hold point) was approximately 100 seconds. It was considered that this was sufficient time for the heating block and the powdered sample to reach temperature equilibrium. The spectra were acquired by coaddition of 64 scans for the whole temperature range (approximate scanning time 45 seconds), with a nominal resolution of 4 cm⁻¹. Good quality spectra can be obtained providing the sample thickness is not too large. If too large a sample is used then the spectra become difficult to interpret because of the presence of combination and overtone bands. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the Spectracalc software package (Galactic Industries Corporation, Salem, NH, USA).

2.4 *DTA/TGA.*

Differential thermal and thermogravimetric analyses of the <2 μ nontronites were obtained using a Setaram DTA/TGA instrument operating at 1.0°C per minute from ambient temperatures to 700°C.

3. Results and discussion

Two nontronites from Hohen-Hagen and Garfield have been extensively used as reference clays [15] but are becoming very difficult to obtain. Recently, two nontronites were discovered at the Uley Graphite mine near Port Lincoln, South Australia, within heavily weathered granulite facies schist, gneiss and amphibolite of Palaeoproterozoic age [25]. Geologic evidence indicates two distinct nontronites are present: a green nontronite associated with weathered biotite schist bands, and a brown nontronite filling joints and fractures within the amphibolite composed of anorthite and highly altered alumino-ferro-hornblende [25]. Preliminary mineralogical and chemical analyses support this finding and indicate that the Uley green nontronite is similar in chemistry and structure to the Garfield nontronite, whereas the Uley brown nontronite appears to be significantly lower in aluminium and possibly contains tetrahedrally coordinated iron [25]. This makes this nontronite closer to the Hohen-Hagen nontronite.

The minerals were selected to provide a range of total Fe^{3+} and Al contents. The Fe contents (ignited, Fe_2O_3 basis) are: Uley green 36.49; Garfield 36.4; NG-1, 37.5%; Uley brown 38.1. The aluminium content of the Garfield nontronite 7.54 % and NG-1 nontronite 6.06 %. The aluminium content of the Uley green nontronite and of the Uley brown sample are 8.15 % and 3.02 %. It should be noted that NG-1 and the Uley brown nontronite each contains significant amounts of ferric iron in the tetrahedral sheet. However each of the nontronites studied here contain most of the iron as ferric iron in the octahedral sheet. Thus, based on chemical composition, the Uley smectites are members of the smectite series in which the octahedral aluminium

has been replaced by octahedral ferric iron. It should be noted some of the Fe ($\approx 18\%$) is incorporated in the tetrahedral sheets. Nontronites contain Fe predominantly in the trivalent state. Most of the layer charge originates from the tetrahedral layer with negative 0.91 and -0.18 on the octahedral layer. The interlayer charge is -1.09 . For nontronite, the charges on the octahedral and tetrahedral layers are -0.08 and -0.92 with an interlayer charge of -0.99 . It is generally accepted that nontronite contain Fe predominantly in the trivalent state [27]. The two minerals are very similar in formulation, the major difference being in the iron content.

Infrared absorption spectroscopy of the hydroxyl-stretching region.

Figure 1 displays the infrared absorption spectra of the nontronites and the results of the band component analyses are reported in Table 1. For the Garfield nontronite bands are observed at 3575 , 3424 , 3251 and 3036 cm^{-1} with relative intensities of 21.1, 34.9, 24.8 and 19.0 %. Some variation in both the band position and intensities between the nontronites is observed. Infrared absorption bands are observed for the Uley brown nontronite at 3572 , 3430 and 3262 cm^{-1} with relative intensities of 22.3, 39.0 and 24.9% and for the Uley green nontronite at 3567 , 3426 and 3255 cm^{-1} with 21.9, 50.5 and 23.5 % relative intensity. For the Hohen-Hagen nontronite, bands are observed at 3598 , 3439 and 3221 cm^{-1} with 12.5, 55.8 and 29.9 % relative intensity. The infrared absorption spectra of the Uley nontronites more closely follow that of the Garfield nontronite than that of the Hohen-Hagen nontronite.

The bands at around 3560-3570 cm^{-1} in the spectra of the three nontronites are assigned to the hydroxyl stretching vibration of the FeFeOH unit. The relative intensity of this band is greatly influenced by the band at $\sim 3420 \text{ cm}^{-1}$ which is attributed to the hydroxyl stretching frequency of water from the hydrated calcium in the interlayer structure. Thus the relative intensity of the hydroxyl-stretching band of the FeFeOH unit is effected by the amount of water in the nontronites. The band at around 3240 cm^{-1} may be ascribed to the overtone of the HOH water bending vibration observed at 1630 cm^{-1} . In the spectra of the hydroxyl-stretching region of ferruginous smectites a hydroxyl stretching frequency at around 3590 cm^{-1} is observed which is attributed to the AlFeOH unit. However because of the extremely low Al content of these three nontronites, this band is not observed.

In the study of the vibrational spectra of kaolinites, the vibrations of the hydroxyl units function cooperatively as in-phase and out of phase vibrations. The question arises as to whether the FeFeOH and AlFeOH units cooperate as in-phase and out of phase vibrations. The band at 3240 cm^{-1} may be interpreted as the out of phase vibration of the in phase vibration at 3400 cm^{-1} rather than the overtone of the water bending vibration at 1630 cm^{-1} .

3.1 Infrared emission spectroscopy of the hydroxyl-stretching region.

The infrared emission spectra of the Garfield nontronite and the Uley green and brown nontronites are shown in **Figures 2-4**. A comparison of the spectral frequencies of the hydroxyl-stretching for the three nontronites is reported in **Table 2**.

The spectra show the presence of water vapour. This is observed by the superimposition of the high frequency in the 1400 to 1700 and 3300 to 3900 cm^{-1} region. This water vapour is a result of the loss of the hydration water and is more pronounced in the low temperature IES spectra at 200 and 250 °C. Bands observed in the 2950 cm^{-1} region are due to the presence of organics. Three hydroxyl-stretching frequencies for the Garfield nontronite are observed in the 200 °C spectrum at 3692, 3574, and 3478 cm^{-1} . The latter two bands may correspond with the two Raman bands observed at 3574 and 3436 cm^{-1} . However it is probable that these are two different vibrational modes. The Uley brown nontronite shows three bands at 3727, 3574, and 3416 cm^{-1} in the 200 °C spectrum. For Uley green nontronite three bands are observed at 3690, 3585, and 3458 cm^{-1} . All three nontronites have a common emission band at 3574 cm^{-1} , which is assigned to the FeFeOH hydroxyl-stretching vibration. The IES band at around 3700 cm^{-1} is also common to the nontronites and is attributed to FeAlOH stretching vibrations. Another possibility for bands in this position is the attribution to SiOH stretching vibrations. It is not uncommon to observe SiOH vibrations in the 3700 to 3750 cm^{-1} region [18]. At the lower temperatures for emission spectroscopy (200 and 250 °C), bands are also observed at the 3440 and 3200 cm^{-1} positions. The spectra from and above 300 °C, do not show bands in these positions.

The intensity of the 3560 cm^{-1} band decreases as a function of temperature and mimics the dehydroxylation of nontronites as determined by thermal analysis techniques. Dehydroxylation takes place between 400 and 450 °C, when no intensity remains in the hydroxyl-stretching bands. Figure 5 displays the variation of relative intensity of the three nontronites as a function of temperature. The loss of intensity of

the Uley green and Garfield nontronites as a function of temperature are similar. It would appear that the loss of intensity is continuous rather than stepped as with a TGA pattern. The TGA pattern for the three nontronites over the same temperature range is shown in **Figure 6**. Little difference can be observed in the TGA patterns for these three nontronites. A very small perceptible weight change may be observed for the Uley brown nontronite at around 250 °C. It is thought that this weight change is due to the presence of an impurity of ferrihydrite. The reason why there is a difference between the intensity-temperature graphs and the TGA curves may be attributed to the way in which the experiment is carried out. The IES experiment is a step process in which the temperature is ramped to the next temperature and then there is a time arrest before collecting the spectral data. The TGA experiment is a continuous experiment with a constant increase in temperature with time.

Figure 7 reports the DTA patterns of the dehydroxylation of the nontronites over the 200 to 600 °C temperature range. The DTA patterns are in good harmony with both the TGA and the decrease in intensity patterns. The DTA patterns show a second endotherm at around 580 °C. This endotherm is not related to the dehydroxylation of the nontronites since no intensity remains in the infrared spectrum of the hydroxyl stretching bands at this temperature. It is suggested that this endotherm is related to a phase change of the dehydroxylated nontronites.

3.2 *Infrared spectroscopy of the Low frequency region.*

The results of the absorption spectra of the low frequency region are reported in **Table 2**. Bands in this region may be attributed to (a) SiO stretching vibrations.

These vibrations are in the 900 to 1100 cm^{-1} region and are ascribed to FeSiO and SiO units [14,27] (b) The 815-860 cm^{-1} region [27]. These bands are attributed to the hydroxyl-deformation of the FeFeOH unit. (c) Bands in the 520 to 600 cm^{-1} region. These bands are attributed to FeFeOH hydroxyl translational modes. (d) Bands observed around 430 and 490 cm^{-1} are attributed to the SiOFe lattice flexing vibrations. Bands which are observed at 780 and \sim 816 cm^{-1} are attributable to traces of quartz impurities. Table 2 shows a comparison of the infrared absorption and low frequency bands of nontronite. Figures 3-5 show the low frequency region of the three nontronites and the results of the band component analysis are shown in Table 4. The lower detection limit in the IES spectra is 450 cm^{-1} . As a consequence bands measured in the absorption spectra are not observed in the IES spectra. The conclusion may be drawn that the spectra of the low frequency region are very similar. Further the IES spectra show strong resemblance to the absorption spectra. The analyses show bands are observed in similar positions for each of the nontronites. The Uley nontronite shows a broad band at around 1450 cm^{-1} . This band is attributed to the presence of fine particles of calcite. The band starts to disappear at 400 °C and no intensity remains at 600 °C.

Of particular importance in the IES spectra, is the observation of bands in the 770 to 870 cm^{-1} region. This spectral region shows the hydroxyl deformation region and the assignment of bands in this region characterises the chemistry and formulation of the nontronites. The Garfield nontronite shows bands at 870, 844, 817 and 778 cm^{-1} . The 870 cm^{-1} band is assigned to the hydroxyl deformation of the AlFeOH unit. The two bands at 844 and 817 cm^{-1} are attributed to the FeFeOH hydroxyl deformation. It is not known why two hydroxyl bands are observed for the FeFeOH

unit. One possibility is that some form of cis-trans isomerisation of this unit exists. This band has disappeared by 350 °C. This observation fits well the decrease in intensity of the hydroxyl stretching vibration at 3570 cm⁻¹. Here the IES spectra showed a continuous decrease in intensity. The band at 778 cm⁻¹ is attributed to the MgFeOH deformation. The IES spectra of the Uley green nontronite shows bands at 870, 844, 819 and 777 cm⁻¹. The attribution of the bands is the same for all the nontronites. However the spectra clearly show intensity differences for the 844 and 819 cm⁻¹ bands. The Uley brown nontronite IES spectra clearly show bands at 870, 840, 820 and 785 cm⁻¹. Significantly for the Uley brown nontronite, the band at 785 cm⁻¹ shows increased intensity compared with the other nontronites. This band is attributed to the MgFeOH unit hydroxyl deformation. The increased intensity of this band reflects the higher Mg content in the octahedral position. The Hohen-Hagen nontronite spectra show bands at 870, 842, 820 and 788 cm⁻¹. This nontronite also shows intensity in the band at 785 cm⁻¹ [28]. The reason why this band occurs at such low frequencies is that the FeMg pairs sharing OH are preferentially along 010 plane with the OH vector extending in the 100 towards the dioctahedral vacancy. The band is present in both the Garfield and Uley green nontronites but is of very low intensity. A band is observed in all the spectra at ~680 cm⁻¹ and is attributed to the bending vibration of the SiOFe unit.

The role of water in smectites often controls their physio-chemical behaviour for example clay rheology. Infrared spectroscopy is one of the best methods for determining the presence of water through the observation of the water HOH bending mode at 1630 cm⁻¹. Thermal analysis shows that water can be difficult to remove from smectites and water coordinating to the interlayer cation may not come off until

~330 °C. Infrared absorption spectroscopy shows a broad band centred on 1630 cm⁻¹ with a component at ~1675 cm⁻¹. Two different types of water are identified by the presence of these two bands namely hydrogen bonded water and water coordinated to the interlayer cations. **Table 5** reports the analysis of the water bending vibration in the infrared emission spectra for the nontronites as a function of temperature. For each of the nontronites three water bending vibrations are identified: a high frequency band at around 1680 cm⁻¹ attributed to water coordinated to the interlayer cation, a normal frequency band at ~1650 cm⁻¹ attributed to interlayer water and the low frequency band at 1595 cm⁻¹ assigned to non-hydrogen bonded water. The IES spectra show the presence of water up to 400 °C. This water may arise from the water in the hydration sphere of the interlayer cation and the water could also come from the dehydroxylation of the nontronite itself. The frequencies of the water bending modes move to higher wavenumbers with increasing temperature.

4. Conclusions

No difference was observed between the absorption and emission spectra of the nontronites. The nontronites are characterised by three bands in the hydroxyl-stretching region with the band at 3570 cm⁻¹ assigned to the hydroxyl stretching vibration of the FeFeOH unit. Dehydroxylation of nontronites has been determined using both DTA/TGA methods and infrared emission spectroscopy. Infrared emission spectroscopy shows that the dehydroxylation is a temperature-continuous process with the significant loss of intensity of the hydroxyl stretching vibrations in the 400 to 500°C temperature range.

Importantly the technique of infrared emission spectroscopy enables the spectra of the nontronites at elevated temperatures to be determined. Further the IES spectra of the Uley green nontronite are identical to that of the Garfield nontronite. The Uley brown nontronite appears to be intermediate between the Garfield and Hohen-Hagen nontronites in terms of spectroscopy. Thus it is concluded that the Uley nontronites are worthwhile nontronite clay minerals, which might replace both the Garfield and Hohen-Hagen nontronites, which are no longer available, at least from a vibrational spectroscopy point of view.

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	Infrared Absorbance	ν_1	ν_2	ν_3	ν_4
Nontronites	Suggested Assignments	Hydroxyl stretch of FeFeOH unit	OH stretch of water	First overtone of the HOH bend of water	Possible difference band
Hohen-Hagen	Band Centre/cm ⁻¹ Relative Intensity/%	3598 12.5	3439 55.8	3221 29.8	2935 1.7
Garfield	Band Centre/cm ⁻¹ Relative Intensity/%	3575 21.1	3424 34.9	3251 24.9	3036 19.0
Uley brown	Band Centre/cm ⁻¹ Relative Intensity/%	3572 21.9	3430 50.5	3262 23.5	3043 4.0
Uley green	Band Centre/cm ⁻¹ Relative Intensity/%	3566 22.3	3426 39.0	3256 24.9	2998 13.7

Table 1 Infrared absorption bands of the hydroxyl-stretching region of nontronite

Table 2 Infrared absorption and emission bands of nontronite

Infrared absorption spectroscopy				Infrared emission spectroscopy (200 °C)				Suggested Assignments
Garfield Nontronite	Uley Green	Uley Brown	Hohenhagen, Germany 32.2% Fe	Garfield Nontronite	Uley Green	Uley Brown	Hohenhagen, Germany 32.2% Fe	
3575	3572	3572	3598	3573	3585	3574	3597	FeFeOH stretch
				3478	3463	3460	3432	OH stretch of water
3424	3426	3430	3439		3430	3416		OH stretch of water
3251	3255	3262	3221				3232	First overtone of HOH bending
3036	3036	3036	3036			3067	3047	Combination band
1670 1630	1670 1630	1670 1630	1670 1630	1647 1580	1650 1590	1680 1642 1580	1628	HOH bending
				1206	1226			
1132	1131	1131		1136	1165	1131		SiO stretch
1093	1093	1093	1092	1070	1105	1104	1077	SiO stretch
1032	1333	1333	1032		1003	1037	1039	FeSiO stretch

973	972	972	972	974	928	970		SiO stretch
879	880	880	879	893		894	880	AlFeOH deformation
				841		841		FeFeOH deformation
778	777	777	795	804	812	815	793	Quartz impurity
755	755	755					788	MgFeOH deformation
680	680	680	680	671	673	676	693	
656	655	655						
588	568	568		580	593	590		FeOSi bend
547	547	547		478	481	494	487	SiOFe bend
450	450	450	463				458	SiOSi bend (463 is quartz impurity)
429	428	428	429					SiOFe bend Octahedral Fe

Table 3 Bands of the hydroxyl-stretching region of the infrared emission spectra of Garfield nontronite, Uley brown nontronite, Uley green nontronite as a function of temperature.

Nontronites		Temp/ °C	200	250	300	350	400	450	500
Garfield	Band Centre/cm ⁻¹	v ₁	3692	3699	3687	3684	3697	3706	3709
	Relative Intensity/%		6.7	23.7	22.0	21.2	9.4	8.7	9.5
	Band Centre/cm ⁻¹	v ₂	3574	3572	3572	3570	3567	3584	3612
	Relative Intensity/%		38.2	29.4	34.0	33.0	31.6	25.4	18.2
Garfield	Band Centre/cm ⁻¹	v ₃	3478	3512	3523	3518	3452	3427	3440
	Relative Intensity/%		35.7	16.3	19.7	18.8	47.8	47.9	45.0
	Band Centre/cm ⁻¹	v ₄		3389	3433	3418			
	Relative Intensity/%			19.0	13.9	19.7			
Uley brown	Band Centre/cm ⁻¹	v ₁	3727	3714	3735	3710	3708		
	Relative Intensity/%		26.2	4.8	24.9	17.8	13.7		
	Band Centre/cm ⁻¹	v ₂	3574	3576	3576	3578	3580		
	Relative Intensity/%		49.1	86.6	72.0	73.6	66.8		
Uley brown	Band Centre/cm ⁻¹	v ₃	3460	3450			3430		
	Relative Intensity/%		2.0	2.0			9.4		
	Band Centre/cm ⁻¹	v ₄	3416	3390					
	Relative Intensity/%		19.0	6.2					
Uley green	Band Centre/cm ⁻¹	v ₁	3690	3692	3645	3671	3676		
	Relative Intensity/%		29.0	36.8	57.8	14.4	16.0		
	Band Centre/cm ⁻¹	v ₂	3585	3574	3571	3575	3572		
	Relative Intensity/%		48.2	46.7	35.6	49.4	49.5		
Uley green	Band Centre/cm ⁻¹	v ₃	3458	3466	3468	3473	3455		
	Relative Intensity/%		43.8	16.5	6.6	27.3	25.4		
	Band Centre/cm ⁻¹	v ₄				3351	3347		
	Relative Intensity/%					8.9	9.0		

Table 4 Table of the low frequency region of the infrared emission spectra of Garfield nontronite and Uley brown and green nontronites.

Nontronite	Temp/ ⁰ C	200	250	300	350	400	450	500	550	600	650	700	750	800	
Garfield	v ₁	1206	1216	1219	1217	1217	1218	1216	1210	1205	1201	1192	1193	1199	
	v ₂	1136	1143	1146	1148	1151	1154	1154	1149	1142	1135	1117	1107	1109	
	v ₃	1070	1071	1073	1074	1074	1075	1075	1069	1059	1050	1036	1021	1018	
	v ₄	974	973	972	971	972	971	970	961	952	946	938	939	939	
	v ₅	893	897	896	892	888	882	881	869	858	855	871	873	876	
	v ₆	841	841	841	841	841									
	v ₇	804	806	806	812	817	817	813	807	802	799	806	805	805	
	v ₈	671	671	670	670	671	672	672	671	671	671	671	670	671	670
	v ₉	597	597	596	597	599	601	599	587	587	572	587	585	599	
	v ₁₀	580	580	580	580	580	578	570	541	538					
	v ₁₁	555	553	554	554	553	537	528	515	514	528	529	527	524	
	v ₁₂	518	515	519	520	514	504	503	500	501	505	506	506	508	
	v ₁₃	478	478	479	483	487	489	491	492	494					
Uley Brown	v ₁	1131	1131	1131	1131	1133	1134	1134	1146	1147	1161	1172	1174	1178	
	v ₂	1104	1104	1103	1103	1102	1102	1102	1094	1097	1095	1101	1100	1101	
	v ₃	1037	1036	1036	1036	1039	1039	1040	1060	1050	1027	1028	1027	1028	
	v ₄	970	969	968	968	968	967	967	967	964	942	942	941	942	
	v ₅	894	901	902	904	901	900	899	888	890					
	v ₆	841				849	852	853	864	859	869	869	869	869	
	v ₇	815	829	832	830						791	784	782	776	
	v ₈	676	674	674	675	675	675	675	675	675	675	675	674	673	
	v ₉	605	598	598	599	600	601	601	602	602	603	602	602	602	
	v ₁₀	590									540	544	541	544	

	v ₁₁	545	543	540	538	535	531	533	533	528	522	525	526	525
	v ₁₂	513	504	504	510	517	516	517	517	517				
	v ₁₃	494												
Uley Green	v ₁	1227	1225	1224	1221	1220	1220	1220	1220	1221	1221	1221	1221	1221
	v ₂	1165	1164	1167	1166	1167	1167	1167	1167	1167	1167	1167	1167	1167
	v ₃	1105	1104	1106	1107	1107	1107	1107	1107	1107	1107	1107	1107	1107
	v ₄	1003	1007	1006	1005	1005	1005	1006	1006	1005	1005	1005	1005	1005
	v ₅	928	929	931	931	931	931	930	930	930	930	930	930	930
	v ₆								895	895	895	895	895	895
	v ₇	815	813	811	813	814	814	814	805	805	805	805	805	805
	v ₈	673	673	673	674	674	674	674	675	675	675	675	675	675
	v ₃	593	593	591	579	572	572	572	572	572	572	572	572	572
v ₉	481	481	478	479	479	479	479	479	479	479	479	479	479	

Table 5 Bands of the water-bending region of the infrared absorption spectra of nontronites from (a) Hohen-Hagen (b) Garfield (c) Uley brown (d) Uley green

Nontronites		Temperature/ °C	200	250	300	350	400
Garfield	Band Centre/cm ⁻¹	v ₁ /cm ⁻¹		1666	1680	1690	1690
	Relative Intensity/%	%		45	25	13	10
	Band Centre/cm ⁻¹	v ₂	1647		1647	1652	1650
Uley brown	Relative Intensity/%		75		10	21	20
	Band Centre/cm ⁻¹	v ₃	1595	1595	1590	1575	1570
	Relative Intensity/%		25	55	65	66	70
Uley green	Band Centre/cm ⁻¹	v ₁	1680	1684	1680	1690	1690
	Relative Intensity/%		5	12	27	7	5
	Band Centre/cm ⁻¹	v ₂	1653	1643	1640	1638	1637
	Relative Intensity/%		43	51	18	45	28
Uley brown	Band Centre/cm ⁻¹	v ₃	1610				
	Relative Intensity/%		7				
	Band Centre/cm ⁻¹	v ₄	1560	1567	1570	1565	1560
	Relative Intensity/%		32	18	55	41	51
Uley green	Band Centre/cm ⁻¹	v ₁				1674	
	Relative Intensity/%					26	
	Band Centre/cm ⁻¹	v ₂	1650	1653	1659	1632	
Uley green	Relative Intensity/%		72	79	53	11	
	Band Centre/cm ⁻¹	v ₃	1585	1570	1570	1567	
	Relative Intensity/%		15	21	39	6	

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